57

STUDIES ON BINARY DIFFUSION OF THE GAS PAIRS N_2-A, N_2-Xe AND N_2-He

R. PAUL AND I. B. SRIVASTAVA

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32

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ABSTRACT. The mutual diffusion coefficient of N_2-He, N_2-Xe and N_2-A gas pairs over the temperature interval —30°C to 60°C has been determined by allowing the diffusion to take place between two bulbs through a precision capillary tube. Samples of the gas, withdrawn from one of the bulbs at different times, were analysed by using a previously calibrated thermal conductivity analyser. These experimental data have been utilised for calculating the unlike potential parameters on the Lennard-Jones 12 : 6 model. The parameters have been used to calculate D_{12} and are found to reproduce the experimental data satisfactorily. Further, the thermal conductivity of the mixtures is calculated using only the experimental values of D_{12} and other transport properties of pure gases and reasonable agreement with the experimental data is obtained.

INTRODUCTION

The coefficient of mutual diffusion, D_{12} is the most suitable transport property for studying unlike molecular interactions, because, to the first approximation, it depends only on the force field of the unlike molecules. But the experimental data suitable for inter-molecular force determination are scanty, specially for the poly-atomic molecules. Therefore, mutual diffusion data for various pairs of gases are most desirable. With this end in view a series of accurate diffusion coefficient measurements of different gaseous mixtures have been done in this laboratory over a fairly wide range of temperature. Several workers (Srivastava and Srivastava, 1959a, Srivastava, 1959, Srivastava and Barua, 1959) have measured the binary diffusion of inert gases in the temperature range 0°C-45°C by using the two-bulb diffusion method and have used their data to determine the unlike interaction parameters on the Lennard-Jones (12 : 6) model. The same technique was further used by Paul and Srivastava (1961a, 1961b) for measuring D_{12} of binary mixtures containing a diatomic gas, in the temperature range −30°C to 60°C. In the present work, the mutual diffusion coefficients of N_2 with He, A and Xe have been measured in the above temperature range and the experimental data are used for determining the force constants for unlike interaction on the Lennard-Jones (12 : 6) model.

APPARATUS AND THEORY

The two-bulb technique of Ney and Armistead (1947) was employed for measuring the diffusion coefficients. The details of the apparatus, experimental procedure and the theory have been discussed fully by Paul and Srivastava (1961a).

EXPERIMENTAL RESULTS

The gases used were supplied by British Oxygen Company, England and were quoted to be spectroscopically pure, except xenon which contained about 1% krypton.

Constants of the diffusion apparatus :

Volume of bulb I	325 cc.
Volume of bulb II	547 cc.
Length of the diffusion capillary	9·058 cm.
Diameter of the diffusion capillary	0.316 cm.

$$C_1^{\infty} = 0.373,$$

C_1^{∞} is calculated from the initial concentration in the two bulbs, which was further checked for some runs by determining the concentration at an interval of seven times the relaxation time.

TABLE I

Observed concentration of He at different times for N_2-He at $-30°C$

Time in minutes	R in ohms	C_1^t	$C_1^t - C_1^{\infty}$	$\log_{10}(C_1^t - C_1^{\infty})$
0	—	1.000	0.627	1.7973
35	235.8	0.770	0.397	1.5988
51	229.4	0.691	0.318	1.5024
71	222.8	0.616	0.243	1.3856
91	217.1	0.559	0.186	1.2695

Fig. 1 gives the calibration curve for the three gas pairs and Fig. 2 shows the plots of $\log_{10}(C_1^t - C_1^{\infty})$ versus t for N_2– He at all temperatures.

Table II gives the experimental values of diffusion coefficients for different pairs as determined by the present authors, together with the values obtained by other workers, wherever available, and also the calculated values of D_{12}, using the force constants obtained by the authors.

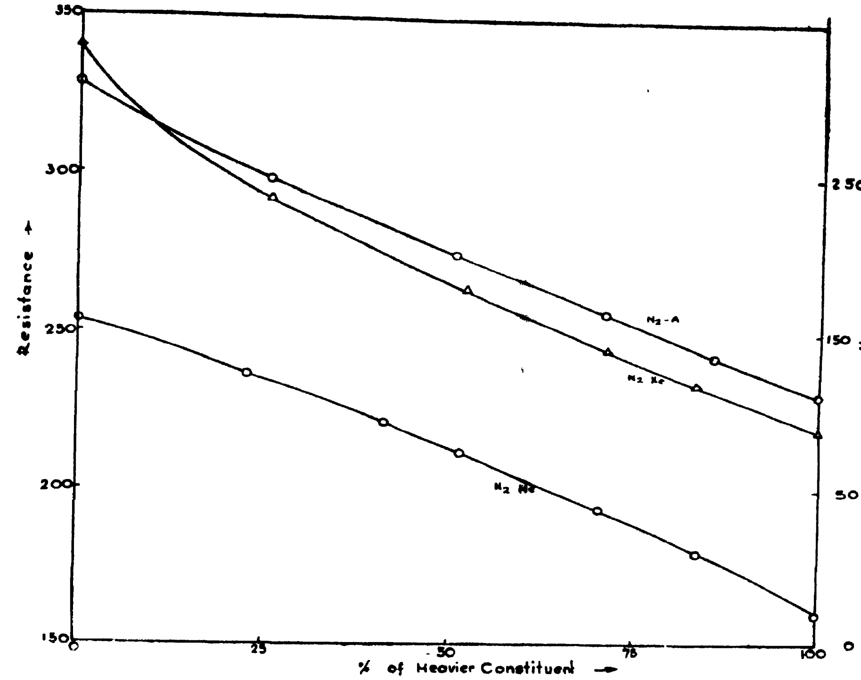

Fig. 1. Calibration curves.

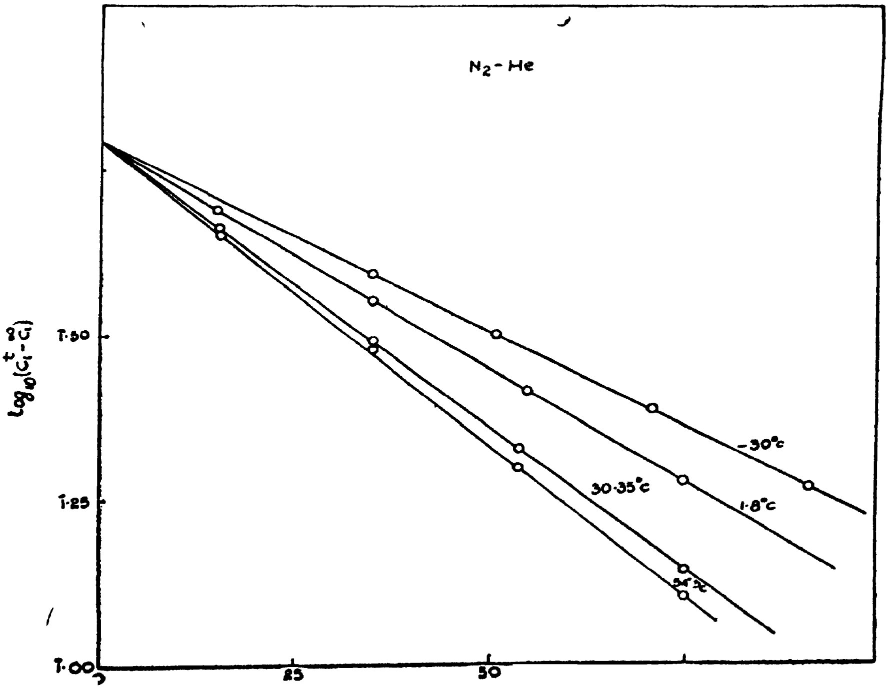

Fig. 2. Plot of log ($C_1^t - C_1^\infty$) versus 't' for N_2–He.

TABLE II

Observed values of the diffusion coefficient in cm^2/sec

Gas mixtures	Temp. °K	Pressure in mm. Hg.	D_p	$D_{atm.}$	Previous[a] work	D_{12} calc. from force constants fitted to diffusion data
	243.2	62.0	5.847	0.477		0.484
	275.0	64.5	7.022	0.596		0.597
	298.16	—	—	—	0.7068	0.6797
N_2 He	303.55	62.1	8.799	0.719	—	0.704
	328.16	—	·	—	0.8212	0.8011
	332.5	65.5	9.410	0.811	—	0.819
	358.16	—	—	—	0.9410	0.9232
	244.2	64.7	1.583	0.1348		0.1363
	274.6	62.2	2.063	0.1689		0.1685
N_2—A	303.55	64.5	2.355	0.1999		0.2018
	334.7	68.3	2.707	0.2433		0.2399
	242.2	63.2	1.027	0.0854		0.0854
	274.6	64.4	1.262	0.1070		0.1078
N_2—Xe	303.45	70.0	1.413	0.1301		0.1299
	334.2	60.3	1.952	0.1549		0.1551

a Rumpol, W.F. (1955)

DETERMINATION OF POTENTIAL PARAMETERS

The various methods for determining the potential parameters from the measured D_{12} values have been fully discussed by Bunde (1955) and Srivastava and Srivastava (1959a), pointing out their advantages and limitations. In the present work, the intersection method of Buckingham (1937) has been used for the determination of the force constants on the Lennard-Jones (12:6) model. As some scatter was found in the intersection points of the curves, the force constants obtained by this method were considered as approximate ones. These approximate values were used to calculate the parameters more accurately by the method of least square fitting. The least square method followed here has been discussed in detail by Paul and Srivastava (1961b).

The force constants determined are tabulated in Table III, together with the values obtained from the combination rules. It is clearly seen that the two sets of orce constants agree within the limits of experimental error.

TABLE III

Potential parameters on the Lennard-Jones (12 : 6) model from the experimental data

Gas pair	Present work	From combination rules
N_2-He		
ε_{12}/k (°K)	35.44	30.58
σ_{12} (Å)	3.129	3.129
N_2-A		
ε_{12}/k (°K)	107.03	106.5
σ_{12} (Å)	3.530	3.549
N_2-Xe		
ε_{12}/k (°K)	147.4	144.8
σ_{12} (Å)	3.846	3.868

COMPARISON WITH EXPERIMENTS

(a) *Mutual diffusion coefficient*

The force constants obtained in the present work have been used to calculate the diffusion coefficients, which have been tabulated in Table II. The agreement obtained is excellent. Further, in case of N_2-He where data of other workers (Rumpel, 1955; Walker and Westenberg, 1958) are available upto 1100°K, the diffusion coefficients calculated from our force constants have been compared

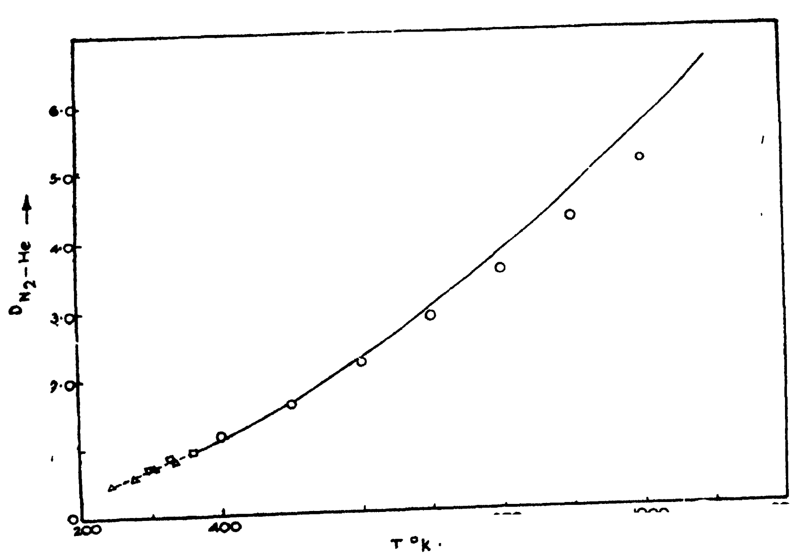

Fig. 3. Temperature variation of the diffusion coefficient of N_2–He system.
——— Interpolated from Walker and Westernberg (1958)
Δ Present work. □ Data taken from Pumpel (1955).
O Calculated values using force constants obtained in the present paper.

graphically with experimental values in Fig. 3. It will be seen from the figure that up to 700°K, the force constants obtained here reproduce experimental values tolerably well. At higher temperatures there are significant deviations, but the force constants determined from the data in the temperature range 250°K to 350°K are not expected to hold good above 700°K.

(b) *Thermal conductivity of mixtures*

The full procedure for the determination of the thermal conductivity of mixtures from the experimental values of the mutual diffusion coefficient and other transport properties of pure component has been given previously (Paul and Srivastava, 1961a).

Fig. 4 presents the experimental values of the thermal conductivity of the mixtures with those calculated by the above method. The agreement is excellent for all the three mixtures. The experimental values of thermal conductivity are taken from Srivastava and Srivastava (1959b) for N_2—A and from Barua (1959) for N_2-He and N_2-Xe.

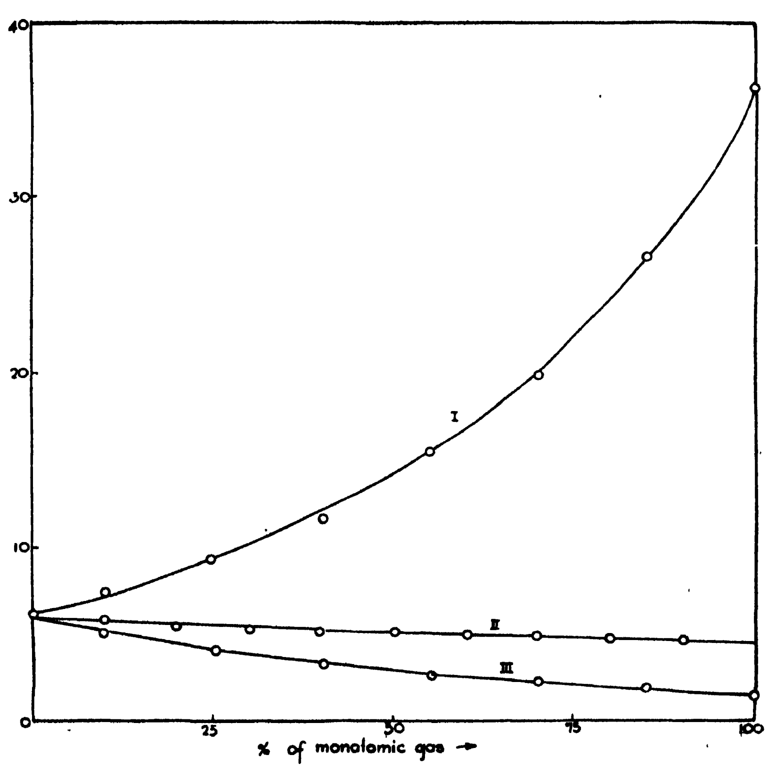

Fig. 4. Comparison of experimental and calculated values of thermal conductivity. I. E_2-He at 30°C, II. N_2-A at 38°C, and III. N_2-Xe at 30°C.

DISCUSSIONS

As the force constants for the pure components are not known very accurately, it is not possible to test the combination rules critically. However, like previous cases, in the present work also, no systematic departure from the combination rule could be observed.

It will be of considerable interest to see how well our force constants reproduce the transport properties other than diffusion and thermal conductivity, but unfortunately, no such data are available at present.

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REFERENCES

Barua, A. K., 1959, *Physica*, **25**, 1275.
Buckingham, R. A., 1938, *Proc. Roy. Soc. (Lond.)*, **A 168**, 264.
Bunde, R. E., 1955, Univ. of Wisconsin, CM-850
Ney, E and Armistead, F. C., 1947, *Phys. Rev.*, **71**, 14.
Paul, R., and Srivastava, I. B., 1961a, *J. Chem. Phys.* In press.
Paul, R., and Srivastava, I. B., 1961b, *Ind. J. Phys.*, In press.
Rumpel, W. F., 1955, Univ. of Wisconsin, CM—851.
Srivastava, B. N. and Srivastava, K. P., 1959a, *J. Chem. Phys.*, **30**, 984.
Srivastava, B. N. and Srivastava, R. C., 1959b, *J. Chem. Phys.*, **30**, 1200.
Srivastava, K. P., 1959, *Physica*, **25**, 571.
Srivastava, K. P., and Barua, A. K., 1959, *Ind. J. Phys.*, **33**, 229.
Walker, R. E., and Westenberg, A. A., 1958, *J. Chem. Phys.*, **29**, 1147.